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(54) BIODEGRADABLE THERMOFORMING SHEET-SHAPED MATERIAL AND CONTAINER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide biodegradable thermoforming sheet-shaped materials and containers which can be directly touched with foods or the like due to high hygienic properties and excel is a heat resistant property and an impact resistance property.
SOLUTION: A biodegradable thermoforming sheet-shaped materials is made of a base substrate mainly consisting of a resin mixture. The resin mixture is composed of a polylactic acid polymer and an aliphatic polyester sharing 20% or more in weight of which glass transition temperature is equal to or lower than 0° C and melting temperature is equal to or higher than 80° C. A layer consisting of a polylactic acid polymer is laminated to at least one surface of the base substrate.

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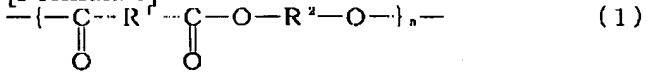
CLAIMS

[Claim(s)]
[Claim 1] The sheet-like object for biodegradability thermoforming characterized by preparing the layer which consists of a polylactic acid system polymer in one [at least] field of the base base material which uses as a principal component the resin constituent with which glass transition temperature blended 0 degree C or less, and the melting point blended aliphatic series polyester 80 degrees C or more with the polylactic acid system polymer 20% of the weight or more.
[Claim 2] The sheet-like object for biodegradability thermoforming according to claim 1 with which said aliphatic series polyester is weight average molecular weight 20,000-300,000, and is characterized by having the structure of the following general formula (1).
[Formula 1]



(1)

(R1 and R2 are the alkylene groups or cyclo alkylene groups of carbon numbers 2-10 among a formula.) n is polymerization degree required to set weight average molecular weight to 20,000-300,000. Even if n R1 or R2 are the same respectively, they may differ. moreover -- the inside of a formula -- ester bond residue -- replacing with -- urethane bond residue and/or carbonate joint residue -- 0- of weight average molecular weight -- it contains 5%.
[Claim 3] The sheet-like object for biodegradability thermoforming given in any 1 term of claims 1-2 to which said polylactic acid system polymer is characterized by being D-lactic-acid:L-lactic acid =100:0-94:6, or 0:100-6:94.
[Claim 4] The container characterized by having carried out thermoforming of the sheet-like object for biodegradability thermoforming of a publication to any 1 term of claims 1-3, and being formed.
[Claim 5] The food-grade container characterized by having carried out thermoforming of the sheet-like object for biodegradability thermoforming of a publication to any 1 term of claims 1-3, and being formed.

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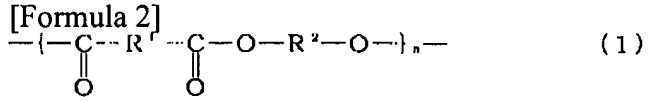
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the sheet-like object for biodegradability thermoforming and a container excellent in thermal resistance and shock resistance about the sheet-like object for biodegradability thermoforming, and a container.
[0002]
[Description of the Prior Art] A close-up of the abandonment processing problem of a plastic has been taken in recent years. Plastic material, such as polyethylene, polypropylene, and polyethylene terephthalate (PET), has much calorific value at the time of combustion, and has a possibility of hurting a combustion furnace during combustion processing, and the polyvinyl chloride with much amount used cannot burn even now because of the autolysis nature. Although laying-under-the-ground processing of the plastic is carried out into soil also including such an ingredient that cannot be incinerated in many cases, these are chemically stable, since there is no biodegradability, remain without almost being decomposed and are accumulated. Therefore, the capacity of a refuse disposal lot will be saturated for a short period of time. Then, the ingredient of biodegradability with it was required, and many researches have been made. [the amount of heat of combustion is low, and safe for the body etc.] Polylactic acid is known as one of them. The amount of heat of combustion is below one half of polyethylene, hydrolysis advances automatically by the inside of soil, or underwater, and, subsequently polylactic acid serves as a harmless decomposition product by the microorganism. Development of containers (moldings), such as a film using current and polylactic acid, and a sheet, a bottle, etc. is performed briskly. however, the film and sheet of polylactic acid -- if it remained as it is, since it was weak and inferior to shock resistance, as for the thermoforming article, the application was limited. On the other hand, although the elution test which guarantees food-sanitation-hygine nature is passed, since the safety of the eluted effluent was not guaranteed, aliphatic series polyester other than polylactic acid had the fault of not being suitable in the application which contacts food and directly.
[0003]
[Problem(s) to be Solved by the Invention] It is in offering the sheet for biodegradability thermoforming and container which this invention was made that the above-mentioned trouble should be solved, and the purpose of this invention was excellent in transparency, and the safety to the body etc. is high, and the use to which food etc. is touched directly is also possible for, and were excellent in thermal resistance and shock resistance.
[0004]
[Means for Solving the Problem] this invention person etc. came to complete this invention, as a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved. That is, the sheet-like object for biodegradability thermoforming of this invention is characterized by preparing the layer which consists of a polylactic acid system polymer in one [at least] field of the base base material which uses as a principal component the resin constituent with which glass transition temperature blended 0 degree C or less, and the melting point blended aliphatic series polyester 80 degrees C or

more with the polylactic acid system polymer 20% of the weight or more. Here, said aliphatic series polyester is weight average molecular weight 20,000-300,000, and can have the structure of the following general formula (1).

[Formula 2]



(1)

(R1 and R2 are the alkylene groups or cyclo alkylene groups of carbon numbers 2-10 among a formula.) n is polymerization degree required to set weight average molecular weight to 20,000-300,000. Even if n R1 or R2 are the same respectively, they may differ. moreover -- the inside of a formula -- ester bond residue -- replacing with -- urethane bond residue and/or carbonate joint residue -- 0- of weight average molecular weight -- it contains 5%.

Moreover, as for the weight average molecular weight of said aliphatic series polyester, it is desirable that it is 150,000-250,000. Moreover, said polylactic acid system polymer can be D-lactic-acid:L-lactic acid =100:0-94:6, or 0:100-6:94. Moreover, the weight average molecular weight of said polylactic acid system polymer can be 100,000-300,000. The container of this invention is characterized by having carried out thermoforming of the above-mentioned sheet-like object for biodegradability thermoforming, and being formed. The food-grade container of this invention is characterized by having carried out thermoforming of the above-mentioned sheet-like object for biodegradability thermoforming, and being formed.

[0005]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The sheet-like object for biodegradability thermoforming of this invention has the layer which becomes one [at least] field of a base base material from a polylactic acid system polymer. For glass transition temperature, 0 degree C or less and the melting point are [the base base material in this invention] aliphatic series polyester (an alicycle group also contains.) 80 degrees C or more to a polylactic acid system polymer. the following -- the same . Let the resin constituent blended 20% of the weight or more be a principal component. That is, the base base material which consists of a resin constituent which contains aliphatic series polyester 20% of the weight or more may be used among the sum total weight of the above-mentioned aliphatic series polyester and a polylactic acid system polymer. Although based also on the manufacture approach, if there are too few rates of aliphatic series polyester, the elongation of a sheet-like object will be less than 10%, and it is weak and is not suitable for anticipated use. In order to improve shock resistance, it is required for the percentage of aliphatic series polyester to be 20% or more by weight, and it is 30% or more preferably.

[0006] A sheet-like object means a sheet or a film here. What is the thin even product with which an even product with the thickness small considering die length and width of face is said thinly [the definition top in JIS and a sheet] and generally, thickness of a film is very small with a product compared with die length and width of face, and the maximum thickness is limited to arbitration, and is supplied in the form of usually and a roll is said (JIS K 6900). Therefore, it can be especially said also in a sheet that the thin thing of thickness is a film. However, since the boundary of a sheet and a film is not certain and it is difficult to distinguish clearly, in this application, the vocabulary of a "sheet-like object" is used as a concept containing both a sheet and a film as above-mentioned.

[0007] The polylactic acid system polymer of the base base material used in this invention and the polylactic acid system polymer which constitutes the layer prepared in one [at least] field of a base base material say what uses as a principal component Pori (L-lactic acid) whose structural unit is L-lactic acid, Pori (D-lactic acid) whose structural unit is D-lactic acid, Pori (DL-lactic acid) whose structural units are L-lactic acid and D-lactic acid, and these mixtures. In this invention, further, you may be a copolymer with other hydroxycarboxylic acid units mentioned later, and little chain elongation agent residue may also be included. If it considers as the configuration of polylactic acid, it is desirable that it is D-lactic-acid:L-lactic acid =100:0-94:6, or 0:100-6:94. Crystallinity becomes low and the polylactic acid of a configuration of separating from this range is inferior to thermal resistance. As a

hydroxycarboxylic acid unit besides the above by which copolymerization is carried out to polylactic acid The optical isomer of a lactic acid (to L-lactic acid, it is L-lactic acid to D-lactic acid and D-lactic acid), A glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 2-hydroxy-n-butanoic acid, 2-hydroxy - Lactone, such as 2 organic-functions aliphatic series hydroxycarboxylic acid and caprolactones, such as 3 and 3-dimethyl butanoic acid, 2-hydroxy-3-methyl butanoic acid, 2-methyl lactic acid, and a 2-hydroxy caproic acid, a butyrolactone, and a valerolactone, is mentioned.

[0008] As a polymerization method of a polylactic acid system polymer, well-known approaches, such as a condensation-polymerization method and a ring-opening-polymerization method, are employable. For example, by the condensation-polymerization method, the polylactic acid system polymer which carries out the direct dehydration condensation polymerization of L-lactic acid, D-lactic acids, or such mixture, and has the presentation of arbitration can be obtained. Moreover, by the ring-opening-polymerization method (the lactide method), a polylactic acid system polymer can be obtained using a suitable catalyst, using the lactide which is the annular dimer of a lactic acid for a polymerization regulator etc. if needed.

[0009] the weight average molecular weight of the polylactic acid system polymer used in this invention is 60,000-700,000 -- desirable -- more -- desirable -- 80,000-400,000 -- it is 100,000-300,000 especially preferably. If molecular weight is too small, practical use physical properties, such as machine physical properties and thermal resistance, will hardly be discovered, but when too large, melt viscosity is too high and inferior to fabrication nature.

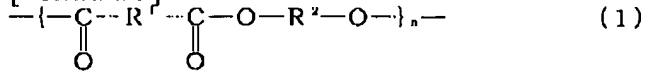
[0010] When the elution test of the food-sanitation-hygine sex test is performed using the polylactic acid system polymer used for this invention, it is a lactide, the oligomer of a lactic acid, and the lactic acid that are eluted in this trial. Even if a lactide is absorbed by the inside of the body, it changes to a lactic acid immediately, and the oligomer of a lactic acid and a lactic acid is used as a food additive, respectively, and the safety to the body etc. is secured.

[0011] The glass transition temperature (it abbreviates to "Tg" hereafter.) is [0 degree C or less and the melting point (Tm) of the aliphatic series polyester used in this invention] aliphatic series polyester 80 degrees C or more. When glass transition temperature (Tg) exceeds 0 degree C, the shock-proof amelioration effectiveness of polylactic acid will be lost, and the melting point (Tm) will be inferior to thermal resistance at less than 80 degrees C. As the above-mentioned aliphatic series polyester, the polymer which uses an aliphatic series dicarboxylic acid unit and an aliphatic series diol unit as a principal component is mentioned. In addition, in this invention, it is desirable to use the aliphatic series polyester of biodegradability. In order to adjust aliphatic series polyester, well-known approaches, such as a direct method and an indirect method, are employable. For example, a direct method is an approach of carrying out direct polymerization and obtaining a high molecular weight object, removing the moisture which generates an aliphatic series dicarboxylic acid unit and an aliphatic series diol unit during the moisture contained in these components, or a polymerization. After carrying out the polymerization of the indirect method to oligomer extent, it is the indirect manufacture approach which carries out macromolecule quantification using a small amount of chain elongation agent like the case of the above-mentioned polylactic acid system polymer.

[0012] As an aliphatic series dicarboxylic acid unit, aliphatic series dicarboxylic acid, such as a succinic acid, an adipic acid, a suberic acid, a sebacic acid, and dodecane diacid, or these anhydrides and derivatives are mentioned. On the other hand, as an aliphatic series diol unit, aliphatic series diols, such as ethylene glycol, butanediol, hexandiol, octanediol, cyclopentane diol, cyclohexane diol, and cyclohexane dimethanol, or these derivatives are mentioned. Each of aliphatic series dicarboxylic acid units and aliphatic series diol units has the desirable thing which has the alkylene group or cyclo alkylene group of carbon numbers 2-10 and which uses 2 functionality compounds as a principal component. Moreover, these aliphatic series dicarboxylic acid unit or an aliphatic series diol unit may use two or more kinds.

[0013] In this invention, it is 150,000-250,000 that the range of the weight average molecular weight of aliphatic series polyester is 20,000-300,000 desirable still more preferably. The property as a polymer is inferior, and if the weight average molecular weight of aliphatic series polyester is too small, if too

large, melt viscosity will become high too much, and the fall of miscibility with polylactic acid and the fall of the extrusion-molding nature when making it a sheet as well as polylactic acid are caused.
[0014] In this invention, the aliphatic series polyester which has the structure of the following general formula (1) can be used preferably.
[Formula 3]



(1)

(R1 and R2 are the alkylene groups or cyclo alkylene groups of carbon numbers 2-10 among a formula.) n is polymerization degree required to set weight average molecular weight to 20,000-300,000. Even if n R1 or R2 are the same respectively, they may differ. moreover -- the inside of a formula -- ester bond residue -- replacing with -- urethane bond residue and/or carbonate joint residue -- 0- of weight average molecular weight -- it contains 5%.
[0015] As aliphatic series polyester used especially suitable for this invention, a polyethylene RENSUBE rate, polyethylene sebacate, a polyethylene decane dicarboxy rate, polybutylene succinate, a polybutylene horse mackerel peat, polybutylene sebacate, polybutylene succinate horse mackerel peats, and these copolymers are mentioned, for example.
[0016] For improvement in melt viscosity, the carboxylic acid, alcohol, or hydroxycarboxylic acid of three or more organic functions can be used for aliphatic series polyester in order to prepare branching. Specifically, polyfunctional components, such as a malic acid, a tartaric acid, a citric acid, trimellitic acid, pyromellitic acid or a pen TAERI slit, and trimethylol propane, can be used. When these polyfunctional components are used so much, it stops being thermoplasticity, the polyfunctional polyester obtained has the structure of cross linkage, even if it is thermoplasticity, the micro gel which has the structure of cross linkage in altitude partially arises, and when it is made a sheet, there is a possibility of becoming a fish eye. Therefore, the rate that these polyfunctional components are contained in aliphatic series polyester needs to be in ********, and is restricted to extent which does not influence the chemical property of a polymer, and a physical property greatly.
[0017] Furthermore, hydroxycarboxylic acid other than non-aliphatic series diol like non-aliphatic series dicarboxylic acid and/or the ethyleneoxide addition product of bisphenol A like a terephthalic acid, and a lactic acid and/or a lactic acid may be used as a little copolymerization component if needed.
[0018] In this invention, it can replace with the above-mentioned aliphatic series polyester or aliphatic series polyester, and the block copolymer (the product by which the ester interchange was carried out in the part, the product containing little chain elongation agent residue, etc. are included) of a polylactic acid system polymer and aliphatic series polyester can be used. This block copolymer can be adjusted by the approach of arbitration. For example, either a polylactic acid system polymer or aliphatic series polyester is separately prepared as a polymer, and the polymerization of the configuration monomer of another side is carried out under existence of this polymer. Usually, the block copolymer of polylactic acid and aliphatic series polyester is obtained by performing the polymerization of a lactide under existence of the aliphatic series polyester prepared beforehand. The point of making aliphatic series polyester living together is only different fundamentally, and a polymerization can be performed like the case where a polylactic acid system polymer is adjusted by the lactide method. In this case, a moderate ester exchange reaction occurs between polylactic acid and aliphatic series polyester, and a copolymer with comparatively high random nature is obtained at the same time the polymerization of a lactide advances. Ester-amide exchange is also generated when the aliphatic series polyester polyurethane which has a urethane bond is used as starting material.
[0019] On each class which constitutes the sheet-like object of this invention, a thermostabilizer, light stabilizer, a light absorption agent, lubricant, a plasticizer, an inorganic filler, a coloring agent, a pigment, etc. can also be added in order to adjust many physical properties.
[0020] The so-called co-extrusion method which carries out melting extrusion at the temperature more than the melting point of this resin as the manufacture approach of the multilayer sheet-like object of this invention using the T die and I die which became the usual multilayer, and a round-head die, and

carries out the laminating of the inside of a dice or the dice at an outlet, the dry laminate which carries out a laminating using adhesives after carrying out melting extrusion separately and sheet-izing, a wet lamination, etc. are mentioned. Especially if the thickness of a sheet-like object is the thickness of extent which can be used for the usual thermoforming technique, it will not be restricted, but specifically, it is desirable that it is the range whose total thickness is about 0.03-2.0mm.

[0021] In this invention, a preheating can be carried out, thermoforming of the sheet for biodegradability thermoforming of this invention can be carried out until it becomes molding temperature by the infrared heater, the hot-platen heater, hot blast, etc., and a container etc. can be formed. As the approach of thermoforming, there are a vacuum-forming method, a plug-assist-forming method, a pressure-forming method, a male-and-female die-forming method, the approach of extending the postforming male which met shaping male type and transformed the sheet, etc. In addition, the configuration of a container, magnitude, etc. shall be suitably chosen according to an application etc. Since the sheet-like object of this invention is covered in the layer which a front rear face becomes from a polylactic acid system polymer, the manufactured container is safe for the body etc. and can be used also as a container into which direct food is put.

[0022]

[Example] Although an example is used for below and being concretely explained to it, this invention does not receive a limit at all by these.

This direction small biaxial extruder whose diameter is 25mm is used. Polylactic acid (the Cargill make, trade name "EcoPLA4040D"), (Example 1) as the aliphatic series polyester concerning this invention -- polybutylene succinate / horse mackerel peat (the Showa High Polymer Co., Ltd. make --) After carrying out mixed fusion of a trade name "Bionolle #3003" and the glass transition temperature of -45 degrees C by 70/30 of weight ratios, it extruded in the strand configuration at 210 degrees C, and the pellet was produced. The single screw extruder with a diameter of 65mm was used as an extruder for middle lamellas, and the single screw extruder with a diameter of 40mm and the multi-manifold die were used as an extruder for surfaces. At 210 degrees C, the produced pellet was supplied to the extruder for middle lamellas with a diameter of 65mm, polylactic acid (the Cargill make, trade name "EcoPLA4040D") was supplied and extruded to the single screw extruder for surfaces with a diameter of 40mm, it quenched with the casting roll after that, and medium-rise thickness obtained 180 micrometers and the two-sort sheet-like object whose surface thickness is 10 micrometers each and which is the total thickness of 200 micrometers which is three layers. The container with a diameter [of 100mm] and a depth of 30mm was fabricated using the obtained sheet-like object under the molding temperature of 100 degrees C, and the conditions of compacting pressure 0.3MPa with the heating plate contact heating type pressure-forming machine made from CKD. Since a surface consists of polylactic acid, even if the obtained container contacts direct food, it is safe for the body etc. and satisfactory in any way. Moreover, since polybutylene succinate / horse mackerel peat was added 30% of the weight as aliphatic series polyester concerning this invention, the medium-rise base layer was excellent in shock resistance, and after putting 100 cc of water into the obtained container and sealing by HITO seal lid material, even if it dropped the floor of concrete from height of 1m, it did not break. In addition, since it excelled also in thermal resistance, as for the sheet-like object of this invention, it turned out that it is suitable also for thermoforming.

[0023] (Example 1 of a comparison) The sheet-like object of a monolayer with a thickness of 300micro was obtained using the polylactic acid used in the example 1, and the same polylactic acid. The container with a diameter [of 100mm] and a depth of 30mm was fabricated for the obtained sheet-like object by the molding temperature of 100 degrees C, and compacting pressure 0.3MPa like the example 1. Although safety [as opposed to the body etc. in the obtained container] was secured, when the drop test was performed, the container was destroyed like the example 1.

[0024]

[Effect of the Invention] As mentioned above, as explained in detail, according to this invention, the sheet-like object for biodegradability thermoforming and container which safety was high, and could use it, could contact food etc. and directly, and were excellent also in thermal resistance and shock

resistance can be offered.

[Translation done.]